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(54) [Title of the Invention] FLAME-RETARDANT POLYPHENYLENE  
ETHER BASED RESIN COMPOSITION

(57) [Abstract]

[Object] To provide a flame-retardant polyphenylene ether based resin composition which is resistant to melt-dropping during burning.

[Solving Means] A flame-retardant polyphenylene ether based resin composition composed of a polyphenylene ether based resin, an organic phosphorous compound, and microcapsulated polyammonium phosphate particles.

[Claim]

[Claim 1] A flame-retardant polyphenylene ether based resin composition characterized by comprising (A) 100 parts by weight of composition composed of 10 to 90 parts by weight of polyphenylene ether resin and 90 to 10 parts by weight of polystyrene based resin, (B) 1 to 100 parts by weight of organic phosphorous based compound, and (C) 0.5 to 50 parts by weight of polyammonium phosphate in which polyammonium phosphate particles are microcapsulated with a synthetic resin.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to a flame-retardant polyphenylene ether based resin composition composed of a mixture of a polyphenylene ether based resin, an organic phosphorous compound, and a polyammonium phosphate microcapsulated with a synthetic resin, the resin composition exhibiting excellent flame retardancy, excellent heat resistance, and a low level of melt-dropping, having good mechanical properties, and including no halogen.

[0002]

[Description of the Related Art] Polyphenylene ether based resins exhibit excellent mechanical characteristics, electrical characteristics, acid resistance, alkali

resistance, heat resistance, and the like, have low water absorption property and good dimension stability, and therefore, have been widely used as materials for housings and chassis of electrical appliances and OA equipment, e.g., computers and word processors, and the like. In many cases, these materials are required to have a high degree of flame retardancy.

[0003] In general, polyphenylene ether resins have excellent flame retardancy but poor workability and, therefore, are usually used as alloys with styrene based resins. Consequently, the flame retardancy is impaired. It is indispensable to make the resin flame-retardant by addition of a flame retardant. It has been previously known to make the resin flame-retardant by blending an organic phosphoric acid ester compound as a flame retardant.

[0004] However, in recent years, demands for safety against fire has been even more zoomed, and in the U.S.A., the regulation of the UL (Underwriters Laboratories) vertical burning test for flammability of electric appliances, OA equipment, and the like have become severe year and year. Furthermore, the thicknesses of products and components have been decreased for the purpose of weight reduction and achievement of greater economy. Consequently, dropping of seeds for fire may occur during burning, so that other products and components are damaged. In order to prevent

this, a material causing no dropping of seeds for fire has been required. For example, almost all materials for both housings and chassis in the field of OA equipment, e.g., printers, personal computers, facsimiles, and copiers, are required to be flame-retardant materials causing no melt-dropping. Likewise, materials for housings of televisions and materials for high-voltage components and power supplies of air conditioners, cellular phones, and the like are also required to be flame-retardant materials causing no melt-dropping during burning.

[0005] A method in which the amount of flame retardant is increased has been known as a technology of preventing melt-dropping during burning. However, there is no economy in using large amounts of inherently expensive flame retardant, and undesirably, generation of gases and deterioration of mechanical properties are facilitated. A resin composition composed of a polyphenylene ether, a flame retardant, and a polytetrafluoroethylene (USP 4355126), a resin composition composed of a polystyrene, silicone, and a carboxylic acid IIa group metal salt (Japanese Examined Patent Application Publication No. 63-10184), and the like have been disclosed as other technologies of preventing dropping. However, the above-described resin compositions exhibit a long burning time and unsatisfactory property for resisting dropping. Therefore, problems are left in practice.

[0006]

[Problems to be Solved by the Invention] The present invention is to provide a flame-retardant polyphenylene ether based resin composition which is effectively resistant to melt-dropping during burning.

[0007]

[Means for Solving the Problems] In consideration of these circumstances, the inventors of the present invention conducted intensive research to overcome the above-described problems in the known technologies and develop a flame retardant polyphenylene ether based resin composition exhibiting an excellent property for resisting melt-dropping during burning. As a result, it was found that melt-dropping during burning was reduced by combining and blending a polyphenylene ether based resin, an organic phosphorous based compound, and a polyammonium phosphate microcapsulated with a synthetic resin and the object was achieved. Therefore, the present invention has been completed.

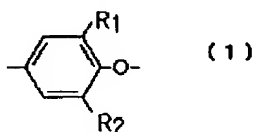
[0008] That is, the present invention provides a flame-retardant polyphenylene ether based resin composition characterized by including (A) 100 parts by weight of composition composed of 10 to 90 parts by weight of polyphenylene ether resin and 90 to 10 parts by weight of polystyrene based resin, (B) 1 to 100 parts by weight of

organic phosphorous based compound, and (C) 0.5 to 50 parts by weight of polyammonium phosphate in which polyammonium phosphate particles are microcapsulated with a synthetic resin.

[0009] The present invention will be described below in detail. The polyphenylene ether resin used in the present invention is a homopolymer having a repeating unit represented by the following formula (1) and/or (2) or a copolymer.

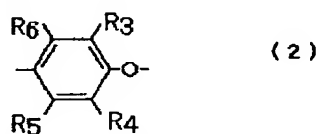
[0010]

[Chemical formula 1]



[0011]

[Chemical formula 2]



[0012] (Where R1, R2, R3, R4, R5, and R6 represent independently an alkyl group having the carbon number of 1 to 4, an aryl group, a halogen, or hydrogen. However, R5 and R6 do not represent hydrogen simultaneously.) Typical examples of homopolymers of polyphenylene ether resins include poly(2,6-dimethyl-1,4-phenylene) ether,

poly(2-methyl-6-ethyl-1,4-phenylene) ether, poly(2,6-diethyl-1,4-phenylene) ether, poly(2-ethyl-6-n-propyl-1,4-phenylene) ether, poly(2-methyl-6-n-butyl-1,4-phenylene) ether, poly(2-ethyl-6-isopropyl-1,4-phenylene) ether, poly(2-methyl-6-hydroxyethyl-1,4-phenylene) ether, and poly(2-methyl-6-chloroethyl-1,4-phenylene) ether. Among them, poly(2,6-dimethyl-1,4-phenylene) ether is particularly preferable.

[0013] The copolymer of the polyphenylene ether resin refers to a copolymer including a phenylene ether structure as a primary monomeric unit. Examples thereof include a copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol, a copolymer of 2,6-dimethylphenol and o-cresol, and a copolymer of 2,6-dimethylphenol, 2,3,6-trimethylphenol, and o-cresol.

[0014] The polyphenylene ether resin used in the present invention may contain other various phenylene ether units as partial structures within the gist of the present invention, while it has been previously proposed that the phenylene ether units have been allowed to present in the polyphenylene ether resin. Examples of units proposed to coexist by a small amount include 2-(dialkylaminomethyl)-6-methylphenylene ether unit and 2-(N-alkyl-N-phenylaminomethyl)-6-methylphenylene ether unit described in Japanese Unexamined Patent Application Publication No. 1-

297428 and Japanese Unexamined Patent Application Publication No. 63-301222. The polyphenylene ether resin may contain a small amount of diphenoquinone bonded in a main chain. Furthermore, polyphenylene ether resins modified by compounds having a carbon-carbon double bond, for example, described in Japanese Unexamined Patent Application Publication No. 2-276823, Japanese Unexamined Patent Application Publication No. 63-108059, Japanese Unexamined Patent Application Publication No. 59-59724, and the like may be contained.

[0015] The method for manufacturing the polyphenylene ether resin used in the present invention is not specifically limited. For example, the polyphenylene ether resin can be produced by subjecting 2,6-xylenol to oxidative coupling polymerization in the presence of a copper amine catalyst based on a method described in Japanese Examined Patent Application Publication No. 5-13966. The molecular weight and the molecular weight distribution are not specifically limited.

[0016] The polystyrene based resin used in the present invention refers to a vinylaromatic polymer, a rubber-modified vinylaromatic polymer, a block copolymer composed of a vinylaromatic polymer block and a conjugated diene polymer block, a block copolymer composed of a vinylaromatic polymer block, in which a part of or entire conjugated diene



polymer block has been hydrogenated, and a conjugated diene polymer block, or the like.

[0017] Examples of vinylaromatic polymers include styrene and other polymers, such as nucleus alkyl-substituted styrenes, e.g., o-methylstyrene, p-methylstyrene, m-methylstyrene, 2,4-dimethylstyrene, ethylstyrene, and p-tert-butylstyrene and  $\alpha$ -alkyl-substituted styrenes, e.g.,  $\alpha$ -methyl styrene and  $\alpha$ -methyl-p-methylstyrene; copolymers of at least one type of them and at least one of other vinyl compounds; and copolymers of at least two types of them. Examples of compounds copolymerizable with vinylaromatic compounds include methacrylic acid esters, e.g., methyl methacrylate and ethyl methacrylate; unsaturated nitrile compounds, e.g., acrylonitrile and methacrylonitrile; and acid anhydrides, e.g., maleic anhydride. Particularly preferable polymers among these polymers are polystyrenes and styrene-acrylonitrile copolymers (hereafter referred to as AS resins).

[0018] Examples of rubber used for the rubber-modified vinylaromatic polymers can include polybutadienes, styrene-butadiene copolymers, polyisoprenes, butadiene-isoprene copolymers, natural rubber, and ethylene-propylene copolymers. In particular, polybutadienes and styrene-butadiene copolymers are preferable. Preferable rubber-modified vinylaromatic polymers are rubber-modified

polystyrenes (hereafter referred to as HIPS) and rubber-modified styrene-acrylonitrile copolymers (ABS resins).

[0019] Examples of block copolymers composed of a vinylaromatic polymer block and a conjugated diene polymer block include styrene-butadiene block copolymers and styrene-isoprene block copolymers. Furthermore, examples of block copolymers composed of a vinylaromatic polymer block, in which a part of or entire conjugated diene polymer block has been hydrogenated, and a conjugated diene polymer block include styrene-butadiene block copolymers, in which a part of or entire butadiene has been hydrogenated, and styrene-isoprene block copolymers in which a part of or entire isoprene has been hydrogenated.

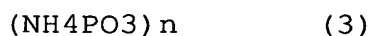
[0020] The organic phosphorous based compound used in the present invention refers to phosphoric acid esters, e.g., tricresyl phosphate, triphenyl phosphate, cresyl-diphenyl phosphate, tris( $\beta$ -naphthyl)phosphate, tris(2,3,6-trimethylphenyl)phosphate, and an ester derived from bisphenol A and diphenyl phosphate, which are known as general phosphorous based flame retardants. These organic phosphorous based compounds can be used alone or in combination of at least two types.

[0021] The blending ratio of the organic phosphorous based compound is varied depending on the ratio of the resin components. If the blending ratio is too small, the flame

retardancy is unsatisfactory, and if too large, the heat resistance and the like of the resin are impaired. In general, the blending ratio is 1 to 100 parts by weight relative to 100 parts by weight of the composition of the polyphenylene ether resin and the polystyrene based resin, more preferably is 3 to 50 parts by weight, and most preferably is 5 to 30 parts by weight.

[0022] The polyammonium phosphate used in the present invention refers to one type of polyammonium phosphate particles microcapsulated with a synthetic resin. Here, the synthetic resin refers to a polycarbodiimide, a polyurethane, a polyisocyanurate, a polyurea, a melamine/formaldehyde-resin, or an epoxide resin.

[0023] The polyammonium phosphates are represented by the following Formula (3).



(In Formula, n represents 200 to 1000)

These polyammonium phosphates microcapsulated with synthetic resins can be used alone or in combination of at least two types.

[0024] If the blending ratio of the polyammonium phosphate microcapsulated with the synthetic resin is too small, the property for resisting dropping during burning is unsatisfactory, and if too large, the impact resistance and the like of the resin are impaired. In general, the

polyammonium phosphate microcapsulated with the synthetic resin is 0.5 to 50 parts by weight relative to 100 parts by weight of the composition of the polyphenylene ether resin and the polystyrene based resin, more preferably is 0.7 to 40 parts by weight, and most preferably is 1 to 30 parts by weight.

[0025] The flame-retardant polyphenylene ether based resin composition of the present invention may contain other additives, for example, impact strength improvers, e.g., an ethylene-propylene elastomer, a styrene graft ethylene-propylene elastomer, a thermoplastic polyester elastomer, an ionomer resin, and a core shell polymer composed of a rubber-like core and a non-rubber-like shell; dropping inhibitors, e.g., Teflon; stabilizers, e.g., plasticizers, other flame retardants, antioxidants, and ultraviolet absorbers; mold release agents; dyes and pigments; or fibrous reinforcements, e.g., glass fibers and carbon fibers; and furthermore, fillers, e.g., glass beads, calcium carbide, and talc, within the bounds of not impairing the effect of the present invention.

[0026] The method for manufacturing the flame-retardant polyphenylene ether based resin composition of the present invention is not particularly specified. The resin composition can be produced by kneading through the use of a kneading machine, e.g., an extruder, a heating roll, a

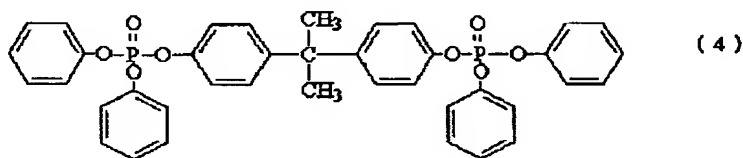
kneader, or a Banbury mixer.

[0027]

[Embodiments] The present invention will be further specifically described below with reference to examples. However, the present invention is not specifically limited to these examples. Organic phosphorous based compounds used in Examples and Comparative examples were organic phosphorous based compounds represented by the following Formulae (4) and (5).

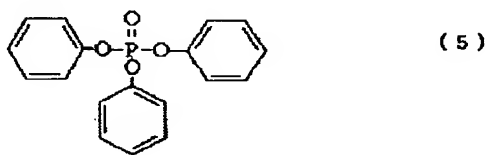
[0028]

[Chemical formula 3]



[0029]

[Chemical formula 4]



[0030] In the following Examples and Comparative examples, the properties of various polyphenylene ether based resins made to become flame-retardant were measured and evaluated by the following method.

(a) Flame retardancy: The measurement and the evaluation were conducted by using 1/16-in test pieces based on 94V-2,

94V-1, and 94V-0 described in items 7 to 10 of "UL94 Safety Standards: Test for Flammability of Plastic Materials for Parts in Devices and Appliances" published by Underwriters Laboratories Inc., U.S.A.

[0031]

[Example 1] Pellets were prepared by mixing 100 parts by weight in total of resin composition composed of 39 parts by weight of poly(2,6-dimethyl-1,4-phenylene) ether (hereafter referred to as PPE) having a limiting viscosity  $[\eta]$  measured in chloroform at 30°C of 0.47, serving as a polyphenylene ether resin, 53 parts by weight of impact-resistant polystyrene resin [trade name Asahi Kasei Polystyrene 492: produced by Asahi Kasei Corporation] serving as HIPS, and 8 parts by weight of polystyrene resin (hereafter referred to as GPPS) [trade name Asahi Kasei Polystyrene 685: produced by Asahi Kasei Corporation] with 14 parts by weight of organic phosphorous based compound represented by the above-described Formula (4) and 1 part by weight of polyammonium phosphate [trade name Hostafrum AP462: produced by Hoechst Japan Ltd.] microcapsulated with a melamine resin, followed by melt-kneading with a twin screw extruder. A 1/16-in test pieces was injection-molded by using the resulting pellets, and evaluation was conducted. The results are shown in Table 1.

[0032]

[Example 2] Pellets were prepared as in Example 1 except that 1 part by weight of polyammonium phosphate microcapsulated with the melamine resin was changed to 5 parts by weight. Thereafter, molding and evaluation were conducted. The results thereof are shown in Table 1.

[0033]

[Example 3] Pellets were prepared as in Example 1 except that the organic phosphorous based compound was changed to triphenyl phosphate represented by the above-described Formula (5). Thereafter, molding and evaluation were conducted. The results thereof are shown in Table 1.

[0034]

[Comparative example 1] Pellets were prepared as in Example 1 except that the polyammonium phosphate microcapsulated with the melamine resin was changed to a polyammonium phosphate [trade name Hostafrum AP422: produced by Hoechst Japan Ltd.] not microcapsulated. Thereafter, molding and evaluation were conducted. The results thereof are shown in Table 1.

[0035]

[Comparative example 2] Pellets were prepared as in Example 2 except that 5 parts by weight of polyammonium phosphate microcapsulated with the melamine resin was changed to a polyammonium phosphate not microcapsulated. Thereafter, molding and evaluation were conducted. The results thereof

are shown in Table 1.

[0036]

[Comparative example 3] Pellets were prepared as in Example 1 except that 1 part by weight of polyammonium phosphate microcapsulated with the melamine resin was changed to 0.3 parts by weight. Thereafter, molding and evaluation were conducted. The results thereof are shown in Table 1.

[0037]

[Table 1]



	Example 1	Example 2	Example 3	Comparative example 1	Comparative example 2	Comparative example 3
PPE	39	39	39	39	39	39
HIPS	53	53	53	53	53	53
GPPS	8	8	8	8	8	8
Organic phosphorous compound (4)	14	14		14	14	14
Organic phosphorous compound (5)			14			
Polyammonium phosphate microcapsulated	1	5	1			0.3
Polyammonium phosphate not microcapsulated				1	5	
Proportion in number of test pieces causing dropping	zero	zero	zero	40 percent	30 percent	20 percent

[0038]

[Advantages] The flame-retardant polyphenylene ether based resin composition of the present invention is a resin composition exhibiting excellent property for resisting dropping as compared with a known flame-retardant resin composition.